

BEHAVIOR OF DIELECTRICS UNDER ALTERNATING STRESS

By

G. M. L. SOMMERMAN, Dr. Eng.

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BEHAVIOR OF DIELECTRICS UNDER ALTERNATING STRESS.*

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G. M. L. SOMMERMAN, Dr. Eng.,†

Formerly of The Johns Hopkins University.

ABSTRACT.

The presence of maxima in the power factor-frequency and power factor-temperature curves of dielectrics has been explained by the Maxwell inhomogeneity theory and the Debye theory of polar molecular orientation. In order to ascertain the true cause of these maxima, a study has been made of the power factor of an essentially non-polar material with and without polar materials in dilute solution over extended ranges of frequency, 65 to 7.2×10^6 c.p.s., and temperature, 2.9° C. to 90° C.

The non-polar solvent is a mixture of paraffins having a pour point at 55° C. Small power factor maxima, 0.0003 in value, shifting over the audio frequency range with temperature variation, are observed for this solvent alone. Adding 3 per cent. phenol gives rise to molecular orientation maxima restricted largely to frequencies above 10^7 c.p.s. At the lower temperatures, these maxima are greatly broadened, so that there is apparently a small contribution at power frequencies. Adding 10 per cent. stearic acid gives similar results. The failure of these maxima to shift to lower frequencies at the lower temperatures is due to the failure of the inner viscosity to increase very much in the solid state. The variation of the inner viscosity is calculated from the reciprocals of the short time conductivities since the degree of ionic dissociation is found to be essentially independent of temperature. The viscosity may be regarded as a function of particle size and varies within the medium. Where power factor maxima shift with essentially undiminished magnitude over a wide frequency range at ordinary temperatures, such as those observed here in the solvent above, it is believed that the cause is the orientation of associated or polymerized polar aggregates of such size as to be affected by the larger viscosity changes approaching the macroscopic.

In the solid and amorphous states, the limited motion of ions leads to an ionic polarization as indicated by absorption curves of relatively large time constants and by high power factors in the low frequency range. The addition of organic acids greatly increases these effects and also increases the final conductivity. The true short time conductivity is largely caused by almost completely dissociated inorganic material.

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† Physical Laboratory, American Steel & Wire Co., Worcester, Mass.

I. INTRODUCTION.

The subject of the loss in dielectrics under alternating stress has incited an enormous amount of both theoretical and experimental work ever since the observation of the pronounced heating in condensers by Siemens in 1864. The reasons for this are several: (1) the complexity of the behavior of the loss and the difficulty of separating the effects of the large number of contributing causes now known to exist; (2) the importance of the loss in its relation to the heating in electrical insulation with its consequent effect on the insulation breakdown strength; (3) the importance of the study of the loss in yielding information concerning the structure of matter.

The sources of dielectric loss under alternating stress may be divided into two general classes: (1) conduction; (2) dielectric absorption. The conduction, or irreversible charge flow, in dielectrics is highly anomalous and may be caused by a number of different types of ions. The last traces of conduction in pure hydrocarbons are evidently due to radioactive ionization as shown by Jaffé.¹ In commercial insulation, however, most of the ions arise from the dissociation of ionizable material, i.e., acids, etc. It was first found by Tank,² and later by Whitehead^{3, 4, 5} and his associates, that the conduction in liquid dielectrics following the sudden application of a direct voltage is constant up to times of the order of 1 second, after which it falls gradually to a low final value. The initial conduction accounts for practically all of the a.c. loss in liquids and the loss is independent of the frequency. The conductivity (conduction for a unit cube per volt) depends on the concentration and mobility of the ions and decreases rapidly with decreasing temperature. There is no measurable effect of conductivity on the dielectric constant for the low values of ion concentrations present in insulators.

Dielectric absorption, or reversible charge flow as a decaying function of time following the sudden application of a constant stress, is the principal source of a.c. loss in solid dielectrics. It also contributes to the dielectric constant in the appropriate frequency range. This property of dielectrics is even more complicated than the conduction and a number of theories have been proposed for its explanation. In all

the simple theories, the absorption current is governed by a first order differential equation and so, all lead to the same form for the decaying function of time, namely, the negative exponential:

$$i_r(t) = EC_0\beta e^{-t/\tau}, \quad (1)$$

where C_0 is the geometric capacity, and τ is the time constant.

Regardless of the nature of the absorption, the dielectric properties for alternating fields may be calculated from the absorption curve by means of the superposition theorem as shown by von Schweidler,⁶ and extended and applied by Whitehead and Baños.⁷ This is perfectly general; the absorption curve is merely used as the response of dielectric to the unit e.m.f., and the a.c. properties follow mathematically. For the negative exponential absorption curve (1) written for unit capacity per volt, the expressions for the loss angle, δ , and dielectric constant, ϵ , as functions of frequency, $f = \omega/2\pi$, are

$$\delta = h\omega\tau/(1 + \omega^2\tau^2), \quad (2)$$

$$\epsilon = \epsilon_0[1 + h/(1 + \omega^2\tau^2)], \quad (3)$$

where h is the absorption constant equal to $\beta\tau$, the area under the absorption curve, and ϵ_0 is the dielectric constant at infinite frequency. It is assumed here and throughout this paper that h is small, as is usually the case for dielectrics. The loss angle, δ , may then be taken as equal to the power factor, $\sin \delta$. The power factor *vs.* log frequency curve goes through a symmetrical maximum of value, $h/2$ at a frequency, $f_m = 1/2\pi\tau$. Correspondingly, the dielectric constant decreases from $\epsilon_0(1 + h)$ to ϵ_0 as the frequency increases, the point of inflexion being f_m . Many experimentally obtained curves show this general behavior, for example, those obtained by Wagner⁸ for a number of waxes, and by Race⁹ for cable compounds.

The theories for the explanation of dielectric absorption and the associated a.c. behavior may be divided into two classes: (1) those dependent on conduction or ionic polarization, chief of which is the inhomogeneity theory of Maxwell, extended by Wagner; (2) those dependent on molecular phenomena only, as represented by the Debye theory of polar

molecular orientation. The inhomogeneity theory as developed by Wagner⁸ gives

$$h_W = 9p(\lambda_1\epsilon_2 - \lambda_2\epsilon_1)^2 / [\epsilon_1(2\epsilon_1 + \epsilon_2)(2\lambda_1 + \lambda_2)^2], \quad (4)$$

$$\tau_W = 8.85 \times 10^{-14}(2\epsilon_1 + \epsilon_2) / (2\lambda_1 + \lambda_2), \quad (5)$$

where material of properties, ϵ_2 , λ_2 , is distributed in concentration, p , in a medium of properties, ϵ_1 , λ_1 . The conductivity, λ , decreases as the temperature is lowered. This does not change h essentially, but it increases τ , so that lowering the temperature shifts the power factor maximum to lower frequencies, as observed. It is necessary, however, to have a conductivity, $\lambda > 10^{-11}$ mho cm.⁻¹ for $f_m > 10$ c.p.s., so that for dielectrics, the contributions from this mechanism can occur only in the low frequency range.

By assigning values of permanent electric moment to molecules, Debye¹⁰ developed a theory of polar molecular orientation which explained many apparent irregularities in the dielectric constants of fluids. The rotation of the polar molecules under alternating stress gives an additional contribution to the dielectric polarization which is inversely proportional to the absolute temperature. Because of the finite time of relaxation of the molecules in liquids, resulting in an increasing frictional restriction of orientation with increasing frequency, the theory predicts a behavior of the type (2) and (3) for polar liquids. The absorption constant, h_D , depends on the concentration and moment of the polar molecules and on the temperature. The relaxation time is

$$\tau_D = 4\pi\eta a^3 / kT, \quad (6)$$

where η = coefficient of inner viscosity; a = radius of polar molecule $\sim 3 \times 10^{-8}$ cm.; k = Boltzmann constant = 1.37×10^{-16} cal. For liquids, the viscosity $\eta \sim 0.01$ to 10 poises, and the frequencies for power factor maxima are in the upper radio frequency range. The best of the early experimental verifications of this anomalous dispersion and energy absorption is that of Mizushima¹¹ on alcohols and glycerin at 5×10^6 to 10^8 c.p.s. To avoid molecular association, Johnstone and Williams¹² studied polar materials dissolved in a heavy non-polar oil at 25° C. and found the effect above 10^7 c.p.s. Since the frequencies for orientation power factor

maxima are so high for liquids, the contribution at power frequencies is negligible, as shown by Hamburger.¹³

If substances were used such that high viscosity values of 10^6 poises and more are attained on lowering the temperature, it would seem that orientation power factor maxima could be shifted to audio and power frequencies. This was first proposed by Kitchin¹⁴ for the rosin and oil-rosin mixtures studied by him. Kitchin and Müller¹⁵ also showed a close correlation between the disappearance of the Kerr effect and the anomalous dispersion, eq. (3), at 60 c.p.s. as well as at radio frequencies. Kirch and Riebel¹⁶ reached the same conclusion. Gemant,¹⁷ however, contended that there are two power factor—frequency maxima, the one at low frequencies being an inhomogeneity effect and the other at high frequencies being an orientation effect. Bormann and Gemant¹⁸ presented data taken at 60 c.p.s. on substances dissolved in oils which led them to the same conclusions. The suggestion is also presented in Gemant's excellent treatise on dielectrics.¹⁹ Against this view are the results of Morgan and White^{20, 21} who made complete frequency studies of rosin and ethyl abietate and also several glycols. These studies showed that power factor maxima can shift continuously from 10^5 to 10 c.p.s. The work of Errera²² on ice indicates that orientation maxima can take place at audio frequencies for non-insulators at least.

Since all theories leading to a negative exponential relaxation function (1) result in the same type of a.c. behavior (2) and (3), it is impossible to state the cause of an observed curve from an analysis of its shape. This has been recognized by Whitehead²³ and others. Moreover, it can be shown that even the variations of the time constants, τ_W and τ_D , with temperature change are the same. The time constants are proportional to the viscosity since both the translational mobility of the ions in the inhomogeneity theory and the rotational mobility of polar molecules in the Debye theory are inversely proportional to the viscosity.

II. PURPOSE OF THE PRESENT WORK.

It is apparent that the only way to determine the frequency ranges over which the two mechanisms can con-

tribute is to make a study of a non-polar material alone over extended ranges of temperature (viscosity) and frequency, and then to add to this material small known amounts of pure polar substances and see in which ranges the new effects occur. While much evidence has been presented for the existence of the Debye mechanism at low frequencies, it has all been obtained with materials of unknown composition or with concentrated solutions of polar substances which lead to molecular association. The procedure outlined above eliminates these difficulties, and it is the principal purpose of this paper to present such a study. It has been found that the ionic effects are confined to the low frequency range, that the power factor maxima due to the orientation of simple polar molecules are confined to frequencies above 10^7 c.p.s. at ordinary temperatures, and that larger associated or polymerized polar aggregates probably account for the power factor maxima which shift continuously from high to low frequencies as observed in ^{8, 9, 14, 20}. Study of the nature of the conductivity and other ionic effects has been facilitated through the use of organic acids for the polar substances. Short time d.c. studies have been made to supplement the a.c. studies and these make possible a quantitative study of the variation of the inner viscosity with temperature.

III. APPARATUS AND PROCEDURE.

The measuring apparatus is described in a separate paper.²⁴ Power factor and dielectric constant measurements were made at frequencies of 65 to 5,000 c.p.s. by means of a double shielded series resistance bridge with Wagner ground, while similar measurements were made at 15,000 to 7,200,000 c.p.s. with a resonance-substitution circuit with vacuum tube voltmeter. The power factor sensitivity for the bridge is usually 0.00002 or better, and for the r.f. circuit is usually 0.00005 or better. The dielectric constant can be obtained to within 0.15 per cent. Short time d.c. studies were made with the amplifier-oscillograph developed by Waldorf,²⁵ and long time conductivities were measured by means of a sensitive d.c. galvanometer. The conductivity sensitivity is 5×10^{-15} mho cm.^{-1} per mm. for the former and 4×10^{-18} mho cm.^{-1} per mm. for the latter. The temperature range studied was

2.9° C. to 90° C. and the temperature was maintained to within 0.1° C. during frequency runs. A gold-plated measuring cell was constructed for use in all of the above circuits. The samples were melted and mixed under vacuum in a separate container and admitted to the measuring cell under vacuum. After solidification of the sample, nitrogen was admitted to atmospheric pressure. This procedure removes air and moisture from the samples, and prevents deterioration before and during the measurements.

IV. THE SPECIMENS.

The non-polar material used in these experiments is a mixture of equal parts by weight of two paraffins of the imported, filtered type. The melting points of the individual paraffins are 68–72° C. and 40–42° C., and the mixture passes gradually from a liquid to a mushy state, a slight whitening appearing at 67° C. The cooling curve shows only a slight change at this cloud point and no other decided irregularities. The viscosity increases gradually until at 50° C. an impression can be maintained, at 35° C. the mixture is quite stiff although still workable with the fingers, at 20° C. it is apparently very hard. The viscosity-temperature curve is given subsequently. This material has the following advantages: (1) it is almost completely free of polar impurities; (2) high values of viscosity are attained at ordinary temperatures; (3) the viscosity and density changes are sufficiently gradual to allow experimental investigation. A complete study was made on this material alone as specimen 1. In order to check some very small power factor maxima, another sample was studied as specimen 2. A further investigation of the nature of these maxima led to the study of samples of the individual paraffins and these were designated as specimens 5 and 6.

Specimen 3 consisted of a 3 per cent. (by weight) solution of phenol, C_6H_6O , M. P. 41° C., in the paraffin mixture. Phenol is a good example of a small polar molecule having an average value of electric moment, 1.70×10^{-18} e.s.u.,²⁶ and it is obtainable in a very pure state. The anomalous dispersion of a solution of a polar substance in a non-polar solvent may be calculated from the equations given by

Debye¹⁰

$$[(\epsilon_1 - 1)/(\epsilon_1 + 2)][(M_1x_1 + M_2x_2)/\rho] = P_1x_1 + P_2x_2, \quad (7)$$

$$P_1 = P_{01} + \mu^2/1.625 \times 10^{-40}T, \quad (8)$$

and the equation

$$[(\epsilon_0 - 1)/(\epsilon_0 + 2)][(M_1x_1 + M_2x_2)/\rho] = P_{01}x_1 + P_2x_2, \quad (9)$$

where ϵ_1 and ϵ_0 are the dielectric constants of the mixture at zero and infinite frequencies, respectively; M_1 and M_2 are the molecular weights, x_1 and x_2 the mol fractions, and P_1 and P_2 the polarizations of the solute and solvent, resp.; and P_{01} is the polarization of the solute at infinite frequency. If eq. (9) is subtracted from eq. (7) and $P_1 - P_{01}$ substituted from eq. (8), and if the weight fractions X_1 and X_2 are introduced in place of the mol fractions, one obtains the relation

$$\frac{\epsilon_1 - \epsilon_0}{(\epsilon_1 + 2)(\epsilon_0 + 2)} = \frac{1}{3} \cdot \frac{\mu^2}{1.625 \times 10^{-40}T} \cdot \frac{\rho X_1}{M_1}. \quad (10)$$

This allows the dispersion for the mixture, $\epsilon_1 - \epsilon_0$, to be calculated in terms of known solute and mixture quantities. Since no solvent quantities are involved, the relation (10) is a useful one in dispersion experiments where the molecular weight of the solvent is not known. In the present case, $\mu = 1.70 \times 10^{-18}$ e.s.u., $X_1 = 0.03$, $\rho = 0.815$ g./cc., $\epsilon_1 = 2.09$, $T = 331^\circ$ K., so that $\epsilon_1 - \epsilon_0 = 0.080$. The power factor maximum corresponding to this, as calculated from the general equation

$$\sin \delta_{\max} = (\epsilon_1 - \epsilon_0)/(\epsilon_1 + \epsilon_0) \quad (11)$$

is 0.018, a good value for experimental investigation.

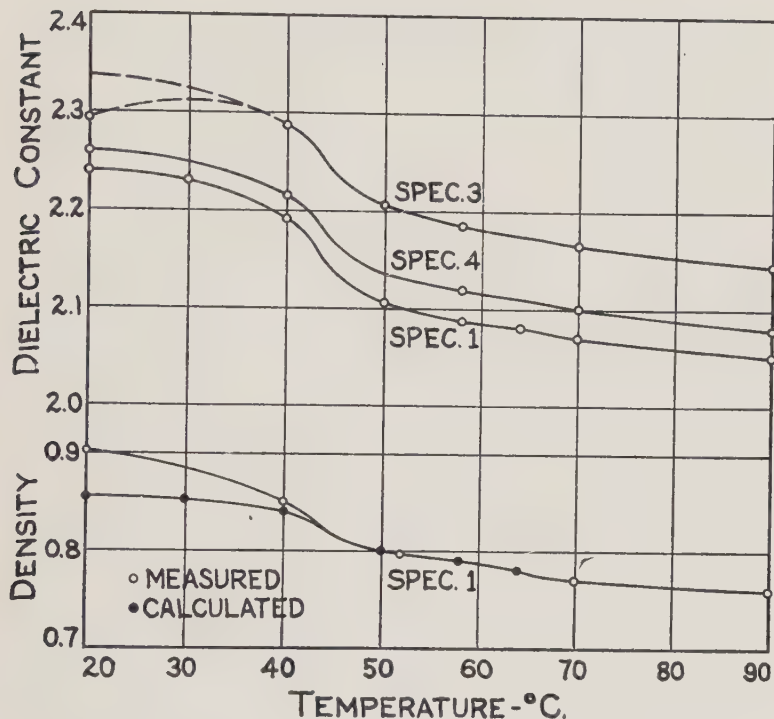
Specimen 4 consisted of a 10 per cent. solution of very pure stearic acid $C_{18}H_{36}O_2$ obtained from Prof. E. E. Reid. This is an example of a polar molecule which is considerably larger than the phenol molecule. A moment value of 0.9×10^{-18} e.s.u. was estimated from values for the lower straight chain acids, and, on solving eqs. (8), (9), (10), (11), the power factor maximum is found to be 0.006.

V. RESULTS.

A. Specimens 1-6.

The density-temperature curve of the solvent alone, presented in Fig. 1, shows the gradual change in density which obtains for the mixture of paraffins. The dielectric constant-temperature curve varies correspondingly. In fact, the varia-

FIG. 1.



Variation with temperature of the dielectric constant at 5,000 c.p.s. and the density.

tion of the effective density of the solvent in the cell may be calculated from this curve, through the use of the relation

$$\rho_{\text{eff}} = K(\epsilon - 1)/(\epsilon + 2). \quad (12)$$

These calculations show that because of the gradual contraction, the material completely fills the cell for temperatures down to about 43° C. Below this, the cell is not completely filled, due evidently to the formation of voids. The densities

of specimens 3 and 4 vary in a similar manner to that of specimen 1, but are about 1 per cent. higher. The higher values of dielectric constant obtained for these specimens in the liquid and amorphous states are due mostly to the orientation of the polar molecules as calculated from eq. (10), although about 0.010 of the difference is caused by the increased densities. At temperatures below 40° C. there is evidently a partial crystallization of the polar solute as indicated by the smaller differences in the dielectric constant curves. This effect will be discussed later in some detail.

FIG. 2.

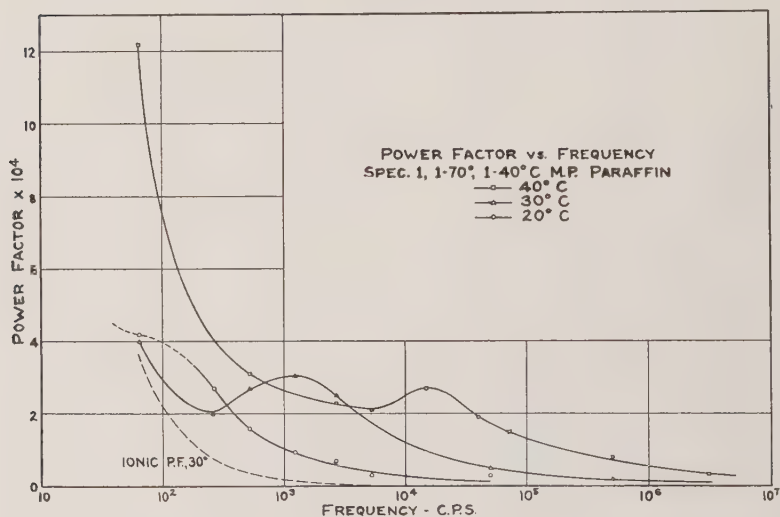
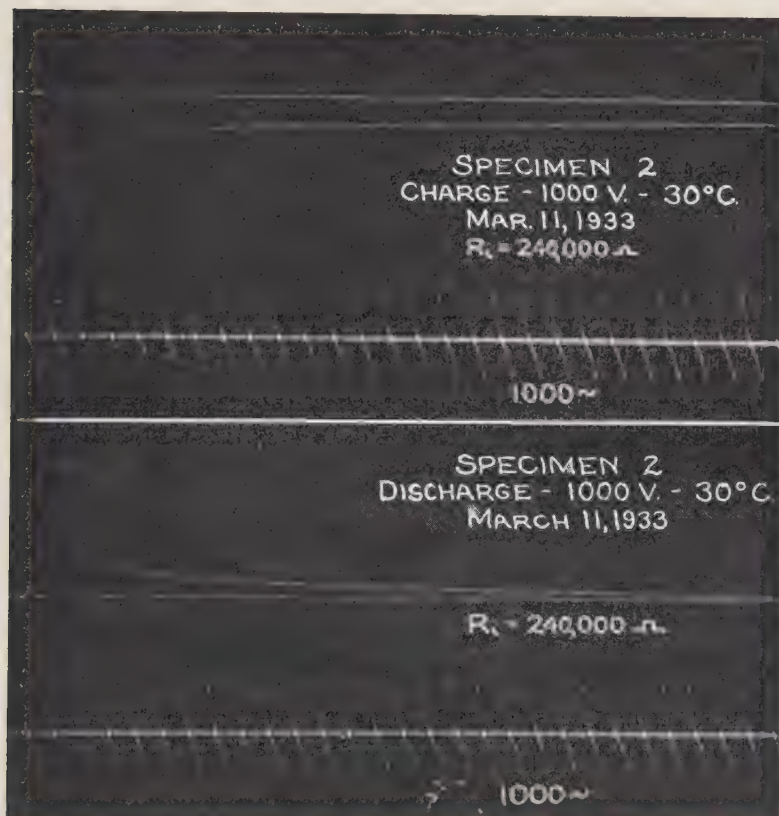


Figure 2 shows the variation of power factor *vs.* frequency at 20° C., 30° C., and 40° C. for specimen 1, the paraffin solvent alone. These power factor curves are made up of two parts: (1) a component caused by ionic phenomena, which decreases as the reciprocal of the frequency; (2) a power factor maximum of value 0.00029. This maximum, the smallest of this type yet reported, was first observed at 30° C. at about 1,300 c.p.s. Raising the temperature to 40° C. shifts the maximum up to about 16,000 c.p.s., while lowering the temperature to 20° C. shifts it down to about 100 c.p.s., a change of frequency of about 13-fold in each case. Above

40° C. the maximum disappears. These curves are somewhat broader than the theoretical curve, eq. (2), but not greatly so. The anomalous dispersion corresponding to this maximum is less than 0.002 which is within the limit of accuracy of the measurements.

FIG. 3



Ionic polarization absorption and short time conduction in paraffin at 30° C.

The ionic losses increase rapidly as the temperature rises. At 70° C. and above (liquid state) they are entirely due to conduction, but with the gradual solidification below 67° C., ionic polarization appears along with the conduction. Figure 3 presents oscillograms showing the charge and discharge curves at 30° C. The time constants of the absorption curves

are so large that the power factor maxima corresponding to them lie considerably below 65 c.p.s. Therefore, above 65 c.p.s., the power factor contribution from this source varies inversely with the frequency (see eq. 2) or the same way as that due to conductivity, δ_λ , which is

$$\delta_\lambda = \lambda / 8.85 \times 10^{-14} \omega \epsilon. \quad (13)$$

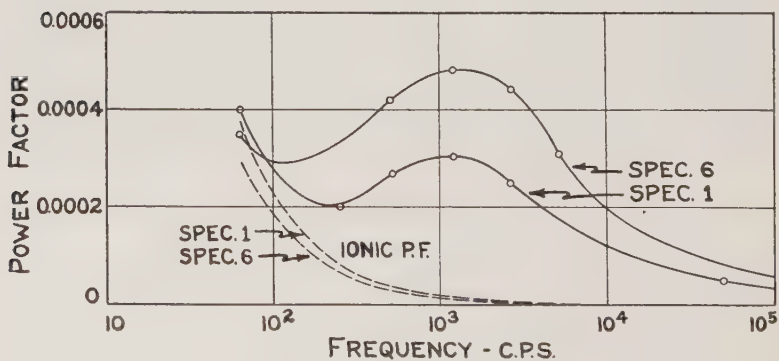
The oscillograms show the appreciable conduction (charge minus discharge) current which greatly exceeds the long time value, the behavior shown by liquids. Values of initial and final conductivities at various temperatures are given in Table I.

TABLE I.
Initial and Final Conductivity in Paraffin.

Temperature, ° C.	Unit: mho cm. ⁻¹ $\times 10^{-17}$.		
	λ_i .	λ_f .	λ_i/λ_f .
90.....	155,000	10,700	15
70.....	79,000	840	94
64.....	50,500	470	108
58.....	26,000	130	200
50.....	10,500	33	320
40.....	3,300	7.8	430
30.....	1,900	3.6	530

The power factor of the 40° M.P. paraffin alone, specimen 6, passes through a maximum of value 0.00047 at about the same frequency as that for the mixture, as shown by Fig. 4.

FIG. 4

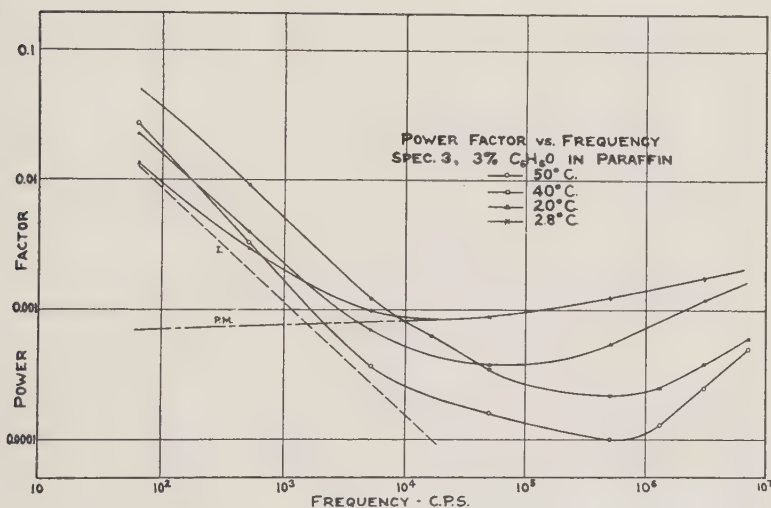


Power Factor vs. Frequency at 30° C. Spec. 1, 1-70°, 1-40° C. M.P. Paraffins.
Spec. 6, 40° C. M.P. Paraffin.

No maximum was observed for the 70° M.P. paraffin alone. Since the mol fraction of the 40° paraffin is about 62 per cent., the effect of mixing the paraffins on the power factor maximum is simply one of dilution of an impurity already present in the 40° paraffin and is not a layer dielectric effect. It will be shown later that this impurity is probably in the form of polar aggregates.

The power factor-frequency curves at 50° C., 40° C., 20° C., 2.8° C., for specimen 3, 3 per cent. phenol, have been plotted in Fig. 5 with logarithmic scales in both power factor

FIG. 5.



and frequency. For these coördinates, the hyperbola representing the variation of the power factor due to ionic effects becomes a straight line of negative slope, and also the rising parts leading to power factor maxima are straight lines of positive slope. In analyzing these curves, it is necessary to remember that they are the combined results of as many as four contributing phenomena.

Adding the phenol produces two effects: (1) the magnitudes of the ionic phenomena, as indicated by the power factor at low frequencies, are greatly increased because of the partial dissociation as an organic acid; (2) power factor

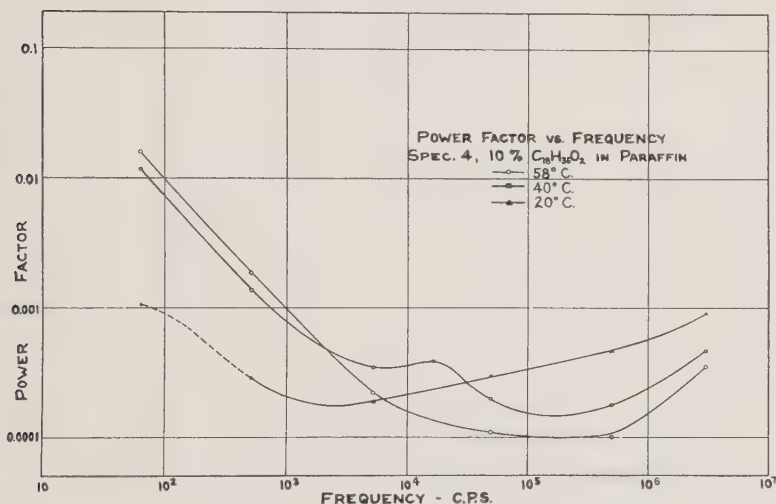
maxima are found at high frequencies due to the orientation of the polar molecules. Other types of polar molecules, such as chlorbenzene, would produce only the second effect. It is seen that even though the temperature is lowered to 2.8°C. , these orientation maxima remain above 7.2×10^6 c.p.s. and only the rising portions can be observed. Lowering the temperature, and hence greatly increasing the apparent viscosity, seems to broaden the maxima, as seen from the decreasing slopes of the curves. The tendency to shift to lower frequencies is slight. The 2.8°C. curve may be broken up into two components: (1) a hyperbolic decreasing component due to ionic effects; (2) a very gradually rising component of about 0.0007 at 60 c.p.s. and 0.0022 at 7,200,000 c.p.s. due to orientation. These are indicated by the broken curves in Fig. 5.

One observed phenomenon that is probably an orientation effect at low frequencies is the following. After lowering the temperature to 20°C. , the dielectric constant at low frequencies was found to be high, 2.7, and anomalous dispersion with an attendant broad power factor maximum occurred at about 5,000 c.p.s. The dielectric constant gradually decreased to a constant value of 2.286 and the power factor maximum disappeared in two days. Because of the transitory nature of the phenomenon, the data are not given, only the final curve for 20°C. being given in Fig. 5. The mechanism of this behavior is probably the following. Upon cooling, some small phenol crystals, having large electric moment, form. The orientation of these polar aggregates increases the dielectric constant at low frequencies, but since the dipoles are of larger than molecular size, they are restricted from orientation at a relatively low frequency and give rise to a power factor maximum there. As the crystals continue to grow, they become so large that they cannot rotate at all and the whole effect disappears. The dielectric constant data indicate that about half of the phenol crystallizes out in this manner, the value after crystallization being only 0.05 above that for the solvent alone as against 0.10 at higher temperatures. On pouring the material into a glass tube, one can observe the phenol crystallizing out in streaks. Increased local dissociation in these streaks results in ionic effects which increase with

time. The ionic phenomena will be discussed later under comparison of results.

It was thought that by increasing the size of the polar molecules in comparison with the spaces between solvent molecules, restriction of molecular orientation would occur at much lower frequencies. The considerably larger stearic acid molecule was tried for this reason. However, the data for this specimen presented in Fig. 6 show a behavior similar to

FIG. 6.



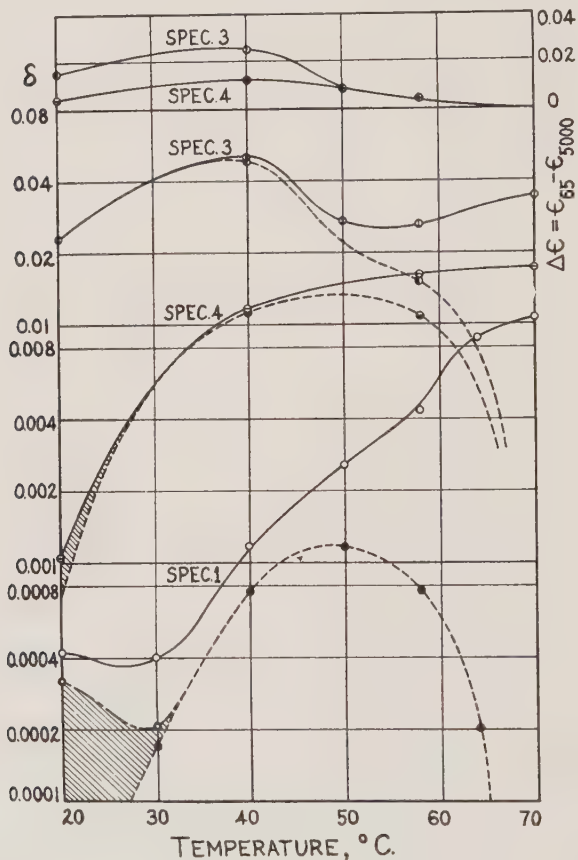
that for the phenol specimen. The ionic effects are somewhat smaller for the stearic acid. The 40° C. curve is especially interesting. It is made up of three parts: (1) at low frequencies, due to ionic polarization; (2) at high radio frequencies, due to polar molecular orientation; (3) a power factor maximum capable of being shifted from high to low frequencies as observed in the solvent alone. This maximum was masked in the phenol specimen by the large ionic effects.

B. Comparison of Results.

The behavior of the ionic phenomena may be seen more clearly from Fig. 7 which presents the power factor at 65 c.p.s. *vs.* temperature for specimens 1, 3, and 4. Short time d.c. measurements were made at all points noted and the curves

analyzed. The power factor contributions due to ionic polarizations absorption are shown by the dotted curves, and the differences are due to conduction. It can be seen that the absorption contribution goes through a maximum in all

FIG. 7.



Power factor, δ , at 65 c.p.s. vs. temperature curves of specimens 1, 3, and 4. The contributions caused by ionic polarization (dotted curves), polar aggregates (hatched areas), and conduction (differences) are shown. The increment in dielectric constant, $\Delta\epsilon$, caused by ionic polarization is also shown.

specimens, being zero in the liquid state, low at low temperatures, and high at 40° C. where the solidification of the paraffin of lower melting point occurs. It is only when the concentration of ions is extremely large and the degree of

heterogeneity great, as in specimen 3, that the *resultant* curve goes through a maximum. Moreover, it is to be noted that increasing the temperature does not shift these maxima to higher frequencies (Fig. 5). The effect of temperature is merely that of a change in the degree of inhomogeneity, p , eq. (4), through changes in the structure of the material, and not a change in the time constant which remains large throughout. The values of the time constants of the absorption curves are given in Table II. These are effective values,

TABLE II.
Effective Time Constants of Ionic Polarization Absorption Curves.

Temperature ° C.	Time Constants in Milliseconds.		
	Specimen 1.	Specimen 3.	Specimen 4.
2.9.....		7.5	
20.....	3.5	12	8
30.....	3		
40.....	7	10	13
50.....	4		
58.....	5	15	29
64.....	8		

the curves being made up of a number of the elementary negative exponential curves, some of which have longer time constants and some shorter. The values do not vary greatly with temperature change. Below 5,000 c.p.s. the ionic polarization in specimens 3 and 4 is sufficient to give a measurable contribution to the dielectric constant. The values of $\epsilon_{65} - \epsilon_{5,000}$ are plotted in Fig. 7. The increments in dielectric constant at various temperatures and also those at various frequencies are roughly proportional to the ionic polarization power factor.

Table III presents values of the initial conductivity, λ_i , and the final conductivity, λ_f , for the three specimens at 58°, 70°, and 90° C. By subtracting the final conductivities from the initial conductivities, the quantities designated as the true short time conductivities, λ_s , are obtained. It is evident that although great increases in the final conductivities are brought about on adding organic acids, the true short time conductivities increase little, if at all. The true short

TABLE III.

Effect of Organic Acids on Conductivity.

Specimen 1. Paraffin.

Specimen 3. 3 per cent. phenol in paraffin.

Specimen 4. 10 per cent. stearic acid in paraffin.

Unit of Conductivity: mho cm.⁻¹ × 10⁻¹⁵.

Temp.	Initial λ_i			Final λ_f			True Short Time $\lambda_s = \lambda_i - \lambda_f$		
	Sp. 1.	Sp. 3.	Sp. 4.	Sp. 1.	Sp. 3.	Sp. 4.	Sp. 1.	Sp. 3.	Sp. 4.
58° C...	260	820	400	1	540	140	260	280	260
70° C...	790	2,650	1,300	8	1,700	360	780	950	940
90° C...	1,540		2,400	110		900	1,430		1,500

time conductivity is an important basic quantity, more so than the total initial conductivity, as will be seen from subsequent discussion.

C. Viscosity.

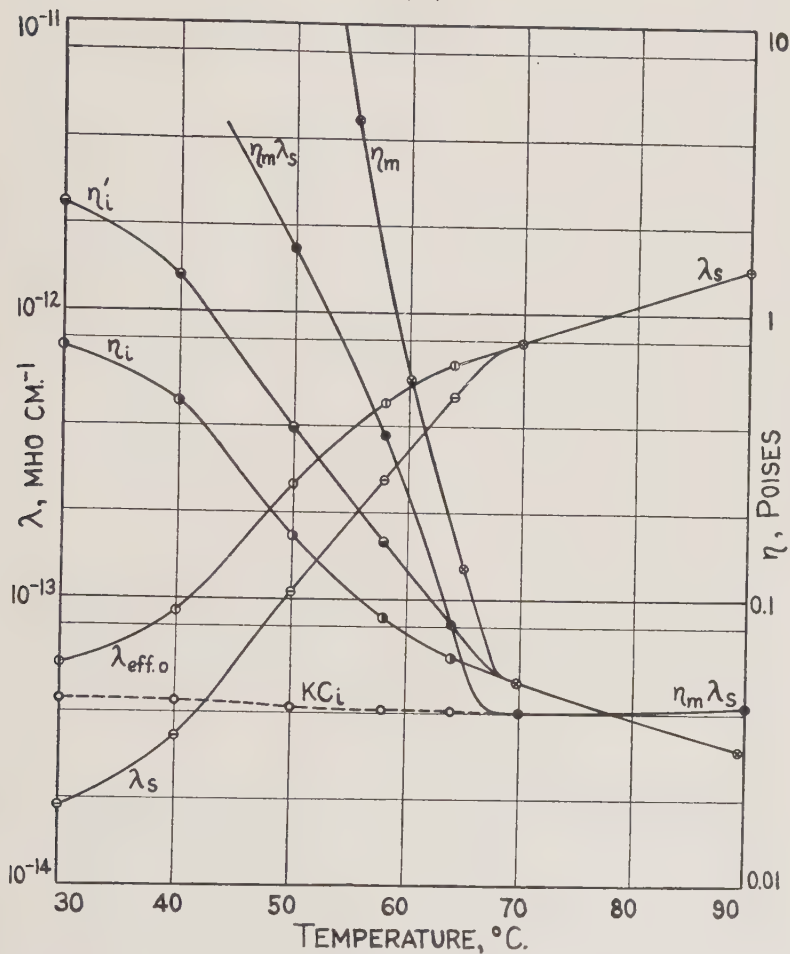
The viscosities of the specimens in the liquid and amorphous states were obtained by a Saybolt viscosimeter and the readings converted to poises. The viscosity-temperature curve for specimen 1 is given in Fig. 8. The values for specimens 3 and 4 are very nearly the same. The sharp rise in this macroscopic viscosity curve below the cloud point at 68° C. is to be noted.

It has been shown by Whitehead ⁵ that the product of the effective conductivity, λ_0 , and the viscosity, η , for a large number of oils, is essentially unaffected by temperature over the range 25°–70° C. It is shown in Fig. 8 that this also holds for the paraffin in the range 70°–90° C. Since the mobility of ions varies inversely as the viscosity and since the conductivity is proportional to the product of the mobility and the number of ions per unit volume, the product, $\eta \cdot \lambda$, is a quantity proportional to the number of ions per unit volume. The fact that the product is constant over a considerable temperature range, leads to the conclusion that the degree of dissociation is independent of temperature.

This fact makes it possible to gain an idea of the variation of the inner viscosity, the viscosity restricting the motion of small particles, in the amorphous and solid states. For a liquid, the inner viscosity evidently varies in about the same

way as the macroscopic viscosity does. Below the cloud point, however, the product $\eta \cdot \lambda$ rises abruptly, which indicates that the macroscopic viscosity is increasing much more

FIG. 8.



Viscosity and Conductivity of Paraffin. λ_s = true short time conductivity; $\lambda_{eff.0}$ = effective conductivity at zero time; η_m = macroscopic viscosity; $KC_i = (\rho/\rho_{70})(\eta_m \lambda_i)_{70}$ $\propto$ concentration of ions; $\eta_i' = KC_i/\lambda_s$, $\eta_i = KC_i/\lambda_{eff.0}$ = inner viscosity.

rapidly than the inner viscosity. This is the same phenomenon as that observed in the classical experiment in physical chemistry,²⁷ which shows the high mobility of ions

in a gel. To find the inner viscosity, η_i , it is assumed that the degree of dissociation, which is later shown to be complete, remains unchanged in the solid state. Then the concentration of ions increases only the small amount due to the higher densities, as shown by the KC_i curve in Fig. 8. By dividing this curve by the conductivity values in the amorphous state, values of inner viscosity are obtained as shown by the curve η_i' .

This treatment assumes that the only resistance to the motion of ions is that due to viscosity. Below the cloud point, the separating out of the heavier paraffins as suspended particles leads to a barrier action preventing the motion of some of the ions. This is manifested by the relatively long time absorption curves which appear in the amorphous state. Immediately after the application of direct voltage, however, all the ions are free to move and are limited only by viscosity. The short time d.c. charge curves have been extrapolated to zero time and the effective conductivities corresponding to these currents have been calculated and plotted in Fig. 8 as $\lambda_{\text{eff. } 0}$. These values divided into the KC_i curve give the η_i curve. It is believed that this curve is a close approximation to the variation of the inner viscosity for the range 40°–90° C. Below 40° C., numerous conducting channels are formed in the paraffin by the increased contraction, and the passage of ions occurs through these and so is not limited by viscosity. This explains the decreasing slope of the η_i curve below 40° C.

VI. DISCUSSION.

A. Power Factor Maxima Due to Dipole Orientation.

The failure of the Debye maxima to shift rapidly to lower frequencies as the temperature is lowered is evidently due to the comparatively small increase in the inner viscosity, η_i . For example, at 50° C., the macroscopic viscosity has risen to 165 poises, which is 3,200 times the 70° C. value, whereas the inner viscosity at 50° C. is only 3 times its 70° value. Moreover, dispersion experiments on liquids, such as water, indicate that even there the inner viscosity may be only about 1 per cent. of the macroscopic value. A number of writers have made statements to the effect that the inner viscosity in very viscous materials is probably less than the

apparent value, and the conductivity data and analysis presented above give quantitative evidence of this.

Onley and Williams,²⁸ working in the range 156 to 17.5 meters and at temperatures of 25° C. and 10° C., have measured a number of polar materials in various solvents of viscosities of 100 poises and greater, yet no appreciable dispersion was observed in the cases where the solute existed in molecular form. The power factor measurements in the present experiments indicate a dispersion which is too small to measure as such, the greatest values being about 0.001.

The slope of the rising portion of the theoretical mono-disperse log power factor-log frequency curve is unity. The fact that the slopes of the experimental curves become less and less with decreasing temperature shows definitely that the curves are becoming increasingly broad. That is, as the temperature is lowered, the relaxation times, τ , of a small but increasing number of the molecules increases, but τ for most of the molecules remains small. From eq. (6), τ is proportional to ηa^3 . It seems probable that a range of values of τ can occur not only through a variation in dipole radius caused by association, but also through a variation of the viscosity restricting the individual molecules caused by differences in the surrounding medium. The broadness of the power factor curves, and hence the range of distribution of η , is small for concentrated solutions of polar material and increases with decreasing concentration as shown by the results of White and Morgan²¹ together with the results presented here.

It appears that the viscosity may be regarded as a function of the particle radius. For a large sphere, η_i assumes the macroscopic value of viscosity. For an electron regarded as an infinitesimal sphere, the absence of a viscosity effect on the electronic conduction in very pure hydrocarbons, as shown by Jaffé,¹ indicates that η_i is infinitesimally small. Finally, for an ion or a small polar molecule, an intermediate value of η_i is encountered. In the Millikan oil drop experiments, departures from Stoke's equation for translational velocity were observed, and these were found to be a function of the ratio of particle radius to the intermolecular distances of the medium. Instead of correcting Stoke's equation for this

ratio, the effect may be taken into account by regarding the correction as applying to the viscosity. The latter method may be preferred by workers in dielectrics since they have already introduced the concept of a lower inner viscosity for dipole orientation. The viscosity may thus be considered as $\eta_i = \eta_i(a/l)$, where l , the intermolecular distance, depends on the solvent and also varies within the solvent.

A number of investigators^{14, 16, 28} have shown that rosin even in dilute solution will cause dispersion at the lower frequencies. It seems that the condition for dispersion at frequencies less than 10^7 c.p.s. and temperatures greater than 0° C. is that the polar material be polymerized or associated. In either case, the radius, a , is large and the relaxation time is increased through the larger values of $\eta_i(a/l)$ in addition to the effect of the a^3 factor. The small power factor maxima in the paraffin alone, Fig. 2, are therefore probably due to the orientation of polar aggregates of large radius. It is certain that they are not due to the orientation of simple polar molecules (Figs. 5 and 6), to ionic polarization (Fig. 7), or to any inhomogeneity produced by mixing paraffins (Fig. 4).

The broadening of any power factor-frequency curve can be represented by a distribution of values $h(\tau)$ in eq. (2). It is interesting to note that the area under the p.f. *vs.* $\ln f$ curve remains proportional to the total dispersion. The power factor at any frequency

$$\delta(\omega) = \int_0^\infty \frac{\omega\tau}{1 + \omega^2\tau^2} h(\tau) d\tau. \quad (14)$$

Substituting $\ln \omega\tau = u$, the area under the $\delta(u)$ curve is

$$\int_{-\infty}^\infty \delta(u) du = \int_{-\infty}^\infty du \int_0^\infty \frac{1}{2} \operatorname{sech} u \cdot h(\tau) d\tau. \quad (15)$$

Integrating first for u (τ constant and ω variable), and then for τ ,

$$\begin{aligned} \int_{-\infty}^\infty \delta(u) du &= \int_{-\infty}^\infty \delta(\ln f) d(\ln f) \\ &= \frac{\pi}{2} \int_0^\infty h(\tau) d\tau = \frac{\pi}{2} \frac{\epsilon_1 - \epsilon_0}{\epsilon_0}. \end{aligned} \quad (16)$$

The application of power factor measurements to dispersion phenomena has also been dealt with in the companion paper.²⁴

B. Conductivity.

The results presented in Table III show that the organic acids ionize in insulating liquids and the ions thus formed contribute greatly to the final conductivity, although the effect on the true short time conductivity is much less and perhaps nil. This means that the true short time conductivity is caused by ions other than organic ions. The fact that the degree of dissociation for this type of ion is essentially independent of temperature has already been pointed out as a consequence of the constancy of the $\eta \cdot \lambda_s$ curve. To be independent of the ionization constants, which increase rapidly with temperature increase, the materials must be completely ionized throughout the temperature range. From the Ostwald dilution law,²⁹ this requires that the ratio of concentration to ionization constant be much less than one. The final conductivity, however, increases much more rapidly than the initial as the temperature rises, as shown by Whitehead⁵ and by the values of λ_i/λ_f in Table I. This means that $\eta \cdot \lambda_f$, and therefore the ionization of organic materials, increases with temperature increase. The ratio of concentration to ionization constant of the organic materials is consequently much greater than that for the material producing the short time ions even where organic material is not purposely added. This difference can be explained by a much greater ionization constant for the short time ions which would mean that they are inorganic (the ionization constant of a material is much less in a dielectric solvent than in water as shown by Gemant¹⁹). These conclusions as to the nature of the ions causing conduction in oils have been previously reached by Herzfeld³⁰ from an analysis of the potential distribution curve of an oil.

C. Ionic Polarization Absorption.

The long time absorption curves and the attendant high power factor in the low frequency range may be regarded as the result of a kind of inhomogeneity mechanism. Actually the mechanism is very much more complicated than those de-

veloped by Maxwell and Wagner, and it seems preferable to regard the phenomena from the microscopic point of view. The action is due to the restricted motion of ions resulting in ionic polarization. Just below the cloud point this restriction is due to the presence of suspended non-conducting particles, while in the solid state it is due to the finite lengths of conducting channels. The restraining force in the first case is viscous, and in the latter case largely adsorptive. The time constant of the absorption depends on this restraining force and on the path length. The restraining force evidently does not vary greatly with the temperature, Fig. 8. As shown by Table III, the time constant may actually decrease with temperature decrease in direct contradiction to the Wagner development. There also appears to be an effect of ion size as seen by comparing the values for specimens 1, 3, and 4, most of the ions in 1 being inorganic. The time constant may be expected to decrease with increasing voltage. While this effect can be observed in the data of Whitehead and Marvin,³¹ it is probably masked to a great extent due to the existence of the large number of exponential relaxations of different time constants. Because of the small effect of temperature on the time constant, this mechanism gives power factor maxima restricted to the very low frequency range, unless a high conductivity layer is deliberately introduced, see Race.³² The absorption constant, h , depends on the concentration of ions as shown in Fig. 7. This has also been shown by Whitehead⁵ for the case of impregnated paper. The dependence of h on the final conductivity has long been noted, see Whitehead and Marvin.³¹

VII. SUMMARY.

1. Measurements of dielectric constant and power factor have been made over the frequency range, 65 to 7.2×10^6 c.p.s. and temperature range 2.8°C. to 90°C. on paraffin and on both phenol and stearic acid in dilute solution in the paraffin. Short time d.c. studies have also been made over the temperature range. Three types of dielectric absorption leading to power factor maxima, and two types of ionic conduction have been studied.

2. The power factor maxima due to the orientation of

simple polar molecules in dilute solution remain above 7.2×10^6 c.p.s. for all temperatures in these experiments although the apparent viscosity attains very high values. Lowering the temperature decreases the frequency for maximum power factor only slightly and its principal effect is to broaden the power factor curve considerably. A small orientation loss may be present at 60 c.p.s. at 20° C. and below. The broadening may be due to a variation of the inner viscosity within the medium as well as to the presence of dipoles of different sizes.

3. The power factor maxima due to ionic polarization or inhomogeneity effects found in the amorphous and solid states remain below 60 c.p.s. The magnitude of the effect is proportional to the concentration of ions present. The behavior is much more complex than that predicted by simple inhomogeneity theories. A tendency for the time constant to increase with rise in temperature and with increase in ion size is observed.

4. The failure of these two types of power factor maxima to shift over extended ranges of frequency with temperature change is due to the failure of the inner viscosity to increase rapidly in the solid state, thus giving only small changes in the rotational mobility of polar molecules in the one case and in the translational mobility of ions in the other. Quantitative results for the variation of inner viscosity with temperature are obtained from the reciprocals of the short time conductivities.

5. In between the high and low frequency ranges, and capable of being shifted from one to the other with essentially unchanged magnitude, is a third type of power factor maximum caused by the orientation of larger associated or polymerized polar aggregates. The viscosity restricting the motion of a particle may be thought of as being a function of the particle radius compared with intermolecular distances.

6. The true short time conductivity is defined as the difference of the initial and final conductivities. The true short time conductivity is largely caused by ions arising from complete dissociation of inorganic material, whereas the final conductivity is caused by organic ions arising from partial dissociation of organic material.

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VITA

George Miller Louis Sommerman, son of George A. and Emma E. Sommerman, was born at Baltimore, Md., on July 2, 1909. He received his preliminary education in the public schools of Baltimore City and the Baltimore Polytechnic Institute, from which he graduated in 1926. Following this, he studied at The Johns Hopkins University, School of Engineering, and there received the degree of Bachelor of Engineering (E.E.), graduating with honor in June, 1929.

From June, 1929, to September, 1930, he was employed as an assistant in the high voltage cable research laboratory at The Johns Hopkins University under Dr. J. B. Whitehead. Then, on receiving a Fellowship of the Tau Beta Pi Association for 1930-1931, he began full time graduate work leading to the degree of Doctor of Engineering given at The Johns Hopkins University. Besides the advanced work in Electrical Engineering under Professors J. B. Whitehead and W. B. Kouwenhoven, he studied in Physics under Professors A. H. Pfund and K. F. Herzfeld, in Mathematics under Professors A. Cohen and F. D. Murnaghan, and in Chemistry under Professor G. H. Cartledge. He received the doctorate in June, 1933. His professional society memberships include: A.I.E.E. (Assoc.); A.A.A.S.; American Physical Society; Sigma Xi.

Aside from the afore-mentioned experience and several engineering positions with the Bell Telephone System, he was employed during the summer of 1931 as assistant physicist in the Research Department of the Consolidated Gas, Electric Light, and Power Co. of Baltimore, Dr. S. Karrer, Director. Here he conducted a research on "Oscillations in Cables Produced by Ionization." On January 1, 1934, he received an appointment to the research staff of the American Steel and Wire Co. at Worcester, Mass. He is associated with the research on impregnated paper cable being conducted at the Physical Laboratory of this company.

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